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Modelling of Polymer Photodegradation for Solar Cell Modules

A Quarterly Technical Progress Report

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LSA Project, Technology Development Area

Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the LSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for LSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

Summary

We have shown that many of the experimental observations in the photo-oxidation of hydrocarbon polymers can be accounted for with a computer simulation using an elementary mechanistic model with corresponding rate constants for each reaction.

For outdoor applications, however, such as in photovoltaics, the variation of temperature must have important effects on the useful lifetimes of such materials.

During this quarter we have researched the data bank necessary to replace the isothermal rate constant values with Arrhenius activation parameters: A (the pre-exponential factor) and E (the activation energy).

Table I summarises the best collection of data that we have assembled to date. Note, however, that the problem is now considerably enlarged since from a theoretical point of view, we now have 51 of the input variables replaced with 102 new parameters. The sensitivity of the overall scheme is such that even after many computer simulations we have not been able to carry out a successful photooxidation simulation with the expanded variable set.

Searching for the important variables and pinning down the inappropriate ones is no easy task for a specific reason: many of the species in the complex process undergo a number of competitive pathways, the relative importance of each being often sensitive to small changes in the calculated rate constant values.

We will continue to pursue this development in the coming quarter.

TABLE I. Elementary Reactions in Polymer Photooxidation and Corresponding Activation Parameters

	Reaction matrix	log A	E_a kcal/mol	Remarks
1.	Ketone $\longrightarrow$ KET*	(-9.2)	0	--
2.	KET* $\longrightarrow$ $SMRO_2$ + SMRCO	8.7	4.8	Ref. 1
3.	SMRCO $\longrightarrow$ $SMRO_2$ + CO	(16.9)	15.0	Ref. 2
4.	KET* $\longrightarrow$ Alkene + SMKetone	(7.8)	2..	Ref. 1
5.	SMKetone $\longrightarrow$ SMKET*	(-9.2)	0	--
6.	SMKET* $\longrightarrow$ $SMRO_2$ + CH_3CO	(12.5)	8.5	Ref. 3
7.	SMKET* $\longrightarrow$ Alkene + Acetone	(8.7)	2.0	Ref. 1
8.	ROOH $\longrightarrow$ RO + OH	(-9.9)	0	--
9.	$\cdot RO_2$ + RH $\longrightarrow$ ROOH + RO_2	9.0	17.0	Ref. 4
10.	$SMRO_2$ + RH $\longrightarrow$ SMROOH + RO_2	9.0	17.0	Ref. 4
11.	SMROOH $\longrightarrow$ SMRO + OH	(-9.9)	0	
12.	SMRO + RH $\longrightarrow$ SMROH + RO_2	9.2	6.2	Ref. 4
13.	RO + RH $\longrightarrow$ ROH + RO_2	9.2	6.2	Ref. 4
14.	RO $\longrightarrow$ $SMRO_2$ + Aldehyde	15.5	17.4	Ref. 4
15.	KET* + ROOH $\longrightarrow$ Ketone + RO + OH	(9.4)	11.6	Ref. 5
16.	SMKET* + ROOH $\longrightarrow$ SMKetone + RO + OH	(9.4)	11.6	Ref. 5
17.	SMRCO + O_2 $\longrightarrow$ SMRCOOO	(13.9)	9.6	Ref. 6
18.	SMRCO + RH $\longrightarrow$ RO_2 + Aldehyde	9.0	7.3	Ref. 7
19.	SMRCOOO + RH $\longrightarrow$ SMRCOOOH + RO_2	9.0	17.0	cf. rxns. 9 and 10
20.	SMRCOOOH $\longrightarrow$ SMRCOO + OH	(-9.9)	0	--
21.	SMRCOO $\longrightarrow$ $SMRO_2$ + CO_2	(14.0)	6.6	Ref. 8

22.	SMRCOO + RH ⟶ Acid + RO_2	9.0	17.0	cf. rxns. 9 and 10
23.	OH + RH ⟶ RO_2 + Water	9.0	0.5	Ref. 9
24.	CH_3CO + RH ⟶ RO_2 + CH_3CHO	9.0	7.3	Ref. 7
25.	CH_3CO + O_2 ⟶ CH_3COOO	(13.9)	9.6	Ref. 6
26.	CH_3COOO + RH ⟶ CH_3COOOH + RO_2	9.0	17.0	cf. rxns. 9 and 10
27.	CH_3COOOH ⟶ CH_3COO + OH	(-9.9)	0	--
28.	CH_3COO + RH ⟶ CH_3COOH + RO_2	(14.0)	6.6	Ref. 8
29.	KET* ⟶ Ketone	(8.0)	0	--
30.	SMKET* ⟶ SMKetone	(8.0)	0	--
31.	KET* + O_2 ⟶ Ketone + SO_2	(13.9)	9.6	Ref. 6
32.	SMKET* + O_2 ⟶ SMKetone + SO_2	(13.9)	9.6	Ref. 6
33.	RO_2 + RO_2 ⟶ ROH + Ketone + SO_2	10.0	3.0	Ref. 4
34.	RO_2 + ROH ⟶ ROOH + Ketone + HOO	9.0	15.3	Ref. 4
35.	HOO + RH ⟶ HOOH + RO_2	(8.5)	(15.0)	K. Ingold, priv. comm.
36.	HOO + RO_2 ⟶ ROOH + SO_2	4.0	1.0	Ref. 4
37.	RO_2 + Ketone ⟶ ROOH + Peroxy CO	5.1	8.9	Ref. 10
38.	Peroxy CO + RH ⟶ PEROOH + RO_2	9.0	17.0	cf. rxns. 9 and 10
39.	PEROOH ⟶ PERO + OH	(-9.9)	0	--
40.	PERO + RO_2 ⟶ DIKetone + ROOH	(9.4)	11.6	Ref. 5
41.	RC_2 + ROOH ⟶ ROOH + Ketone + OH	4.0	1.0	Ref. 4
42.	RO_2 + SMROH ⟶ ROOH + Aldehyde + HOO	9.0	15.3	Ref. 4
43.	RO_2 + Aldehyde ⟶ ROOH + SMRCO	(9.4)	11.6	Ref. 5
44.	RO_2 + RO_2 ⟶ ROOR + SO_2	17.0	16.0	Ref. 4

45.	SO_2	$\longrightarrow$ O_2	(4.8)	0	--
46.	SO_2 + Alkene	$\longrightarrow$ ROOH	(13.3)	10.0	Ref. 11
47.	RO_2 + Alkene	$\longrightarrow$ Branch	8.2	11.6	Ref. 4
48.	$SMRO_2$ + Alkene	$\longrightarrow$ ROOH	8.2	11.6	Ref. 4
49.	RO_2 + QH	$\longrightarrow$ ROOH + Q	7.2	5.2	Ref. 4
50.	KET* + Q1	$\longrightarrow$ Ketone + Heat	(12.9)	9.5	Ref. 12
51.	ROOH + QD	$\longrightarrow$ PRODS	(12.9)	9.5	Ref. 12

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[a] $[O_2] = 10^3$ M (constant); SMProduct = product from chain cleavage.

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